Quantum Phase Transitions in Spin-$\frac{1}{2}$ Frustrated Molecular Cluster: the Numerical Evidence

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By exact diagonalization, we investigate several spin-$\frac{1}{2}$ $J_1 - J_2$ real clusters of molecular scale with different shapes. Our calculations show that when the ratio, η, of next nearest neighbor to nearest neighbor bonds is equal to 1, even the cluster of only 25 sites exhibits the bulk behaviors and has the quantum phase transitions. Two effective critical points are around $J_2/J_1 = 0.3762$ and 0.612 respectively. They are very close to those of the infinite $J_1 - J_2$ square lattice. But, when $\eta \leq 0.85$, the quantum phase transition around $J_2/J_1 = 0.3762$ disappears. By calculating the distributions of the average values of S_i^z, the bulk behaviors are demonstrated graphically. In the intermediate phase, the sites on the corners have distinctly different character from the other sites. The distribution is obviously centralized on the corner sites.

The two-dimensional spin-$\frac{1}{2}$ $J_1 - J_2$ Heisenberg model has been the object of intense investigation through years since the antiferromagnetism can be destabilized by frustrations and it exhibits rich physics and diverse properties. Its Hamiltonian reads

$$H = J_1 \sum_{\langle n.n. \rangle} \vec{S}_i \cdot \vec{S}_j + J_2 \sum_{\langle n.n.n. \rangle} \vec{S}_i \cdot \vec{S}_j, \qquad (1)$$

where $\langle n.n. \rangle$ and $\langle n.n.n. \rangle$ are the sum over the nearest neighbors and next nearest neighbors respectively, $J_1 > 0$ and $J_2 \geq 0$. For the two-dimensional antiferromagnet without frustration ($J_2 = 0$), notwithstanding a mathematically rigorous solution is lacking, it is by now well established that the ground state (GS) has Néel order by many works [9,15]. When $J_2 > 0$, the competition of purely magnetic interactions can lead to the destruction of the long-range order. Many analytical approximations [1–4,9–13] and numerical techniques [5–8] are applied to investigate the phase diagram of the $J_1 - J_2$ model. For small J_2/J_1, the GS will keep Néel order described by a wave vector (π, π) since the frustrations are too weak to destroy it. When J_2/J_1 is large enough, the GS is dominated by the $n.n.n.$ interactions and has a certain type of collinear order described by $(\pi, 0)$ or $(0, \pi)$. But, for intermediate J_2/J_1, the competition between J_1 and J_2 terms results in a spin-liquid GS with a gap to magnetic excitations. The two critical points of phase transition are at $J_2/J_1 = 0.38$ and 0.60 respectively [9–12].

The situation of real cluster, when it has small size, may be different from that of infinite system (the word 'real' means that the free boundary conditions are taken). Especially for real clusters of molecular scale , which has only tens of sites, the boundary effect might be heavy since many sites are on its boundaries. For instance, the 4×4, 5×5 and 6×6 real clusters have 75%, 64% and 56% sites on their boundaries respectively. In order to understand the spin status of real clusters, we introduce

$$Q(\vec{q}) = \frac{1}{N^2} \sum_{(i,j)} \left\langle G \left| \vec{S}_i \cdot \vec{S}_j \right| G \right\rangle \exp(i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)), \qquad (2)$$

as a measure of magnetic orders, where N is the total number of sites, $\vec{r}_i$ and $\vec{r}_j$ the coordinates of sites i and j respectively, $|G\rangle$ represents the GS. At first, we calculate $Q(\pi, \pi)$ of the 5×5 real cluster by exact diagonalization. Our calculation shows that $Q(\pi, \pi)$ decays continuously and monotonically in the region of $J_2/J_1 \sim 0 - 1.0$ (curve (e) in Fig. 2). Especially, unlike the case of the infinite system, the real cluster has no quantum phase transition around $J_2/J_1 = 0.38$. One may think that the cause is too small freedom to form the bulk behavior of spins. It is meaningful to investigate whether the real clusters of molecular scale always keep this property. However, the real cluster with other shape might have different properties due to the boundary effects. If define $\eta \equiv N_{nnn}^{bond}/N_{nn}^{bond}$, where N_{nn}^{bond} and N_{nnn}^{bond} represent the numbers of $n.n.$ and $n.n.n.$ bonds, we notice that $\eta = 1$ for the infinite $J_1 - J_2$ square lattice. η may be an important factor for spin status. In other words, if a real cluster posses a structure of $\eta = 1$, it has possibly the similar quantum transition as the infinite system. When its boundaries are set up along diagonals, the real cluster is able to hold $\eta = 1$. Calculating $Q(\pi, \pi)$ of cluster (a) (Fig. 1), we find that it is quite different from the real 5×5 cluster and $Q(\pi, \pi)$ has a step-like change around $J_2/J_1 = 0.3762$ (Fig. 2). In a very small interval of J_2/J_1, which is less than 4×10^{-4}, $Q(\pi, \pi)$ falls 55%. The abrupt change in such a narrow parameter region means that the small real cluster has possibly the bulk behaviors. *i.e.*, there exists a quantum phase transition around $J_2/J_1 = 0.3762$. Larger $Q(\pi, \pi)$ for $J_2/J_1 \leq 0.3760$ means the Néel-like order [16], whereas small $Q(\pi, \pi)$ for $J_2/J_1 \geq 0.3764$ means its losing. We will give the further evidence for this conclusion. Un-

like the infinite system has $Q(\pi,\pi) = 0$ when the AF long-range order vanishes, here zero $Q(\pi,\pi)$ can not be achieved since the real cluster is finite. In the region $0.3764 \leq J_2/J_1 \leq 1.0$, although $Q(\pi,\pi)$ decays monotonically as J_2/J_1 increasing, it keeps positive. The real frustrated cluster always has a little antiferromagnetism.

Generally, the bulk behavior occurs for these clusters with size large enough. The too small size may lead to its disappearance due to the limitation of freedom. But, our calculations show that when the real cluster of molecular scale keeps $\eta = 1$, it has the bulk properties, especially the quantum phase transition around $J_2/J_1 = 0.38$. Even for the real cluster of 13 sites with the similar shape, there also exists a step-like change of $Q(\pi,\pi)$ within $0.3381 < J_2/J_1 < 0.3886$. It is noticed that cluster (e), *i.e.* the 5×5 real cluster, has $\eta = 0.80$. Three other real clusters (b), (c) and (d) (Fig. 1), which have the same number of sites but the different values of η ($\eta = 0.9$, 0.89 and 0.85 respectively), are investigated. As η decreasing, the jump around $J_2/J_1 = 0.38$ becomes smaller and smaller (Fig. 2). When $\eta \leq 0.85$, the step-like change disappears. Our calculations support the conclusion that η is an important factor for the quantum phase transitions of real clusters and the enhance of η advantages the bulk behavior.

For the frustrated Heisenberg antiferromagnets, when the effect of J_2 terms exceeds that of J_1 terms, the *n.n.n.* interactions may result in the establishing of magnetic orders in its subsystems. If carefully checking the $Q(\pi,\pi)$ curves of these five clusters, one can find inflexions at larger J_2/J_1 (Fig. 2). The difference of their geometric symmetries causes the critical J_2/J_1 values obviously different since for such small clusters, the symmetries may affect heavily the spin-Peierls states of the disordered phase. One notices that same as the infinite square lattice, cluster (a) keeps the rotation symmetry and $\eta = 1$. Its singular point is at $J_2/J_1 = 0.612(\pm 0.002)$. The slope of $Q(\pi,\pi)$ increases when $J_2/J_1 < 0.612$ while deceases when $J_2/J_1 > 0.612$. For convenience, the real cluster is divided into two subsystems A and B (Fig. 1). To understand whether there is quantum transition around $J_2/J_1 \approx 0.612$, it is useful to calculate $Q(\pi,0)$ by formula (2). As shown in Fig. 2, $Q(\pi,0)$ changes rapidly round $J_2/J_1 \approx 0.612$, and it keeps a obviously larger value for large J_2/J_1 than that for small J_2/J_1. It implies the existence of the Néel-like order in both of subsystems A and B while no Néel-like order for the whole real cluster. When $J_2/J_1 < 0.612$, the competition of J_1 and J_2 leads to the disordered GS. Namely, the GS has the character of spin liquid.

The total spin of the GS of cluster (a) is nonzero since it has odd sites. It provide us another way to investigate the spin status. The spin-spin correlations lead to the probability of spin up unequal to that of spin down on each site in the M space, here M is the magnetic quantum number. Consequently $\overline{S_i^z} \equiv \langle G^+|S_i^z|G^+\rangle \neq 0$, here $|G^+\rangle$ involves only the ground states in the $M > 0$ subspaces. (It is quite different from the case of the GS with zero total spin, in which the spin up-down symmetry makes $\overline{S_i^z}$ being zero exactly on each site.) The distribution of $\overline{S_i^z}$ on sites depends on the spin-spin correlations. The study of it is helpful to understand the spin status. Fig. 3 shows the cases of cluster (a) for $J_2/J_1 = 0.37$, 0.40, 0.60 and 0.88 respectively. At $J_2/J_1 = 0.37$, the average value of $\overline{S_i^z}$ for the sites in subsystem A is 2.04×10^{-1} and its statistical fluctuation 5.48×10^{-3}, and that for the sites in subsystem B is -1.41×10^{-1} and its fluctuation 1.43×10^{-3}. *i.e.*, the distribution of $\overline{S_i^z}$ is approximately uniform. It gives a good picture of the Néel-like order. But, when $J_2/J_1 \geq 0.3764$, the distribution is rather different. Fig. 3(b) and 3(c) shows the cases of $J_2/J_1 = 0.40$ and 0.60 respectively. For convenience to describe, we call the sites on four corners as corner sites, and the other 21 sites as the inner sites (Fig. 1). At $J_2/J_1 = 0.40$ and 0.60, $\overline{S_i^z}$ on each corner site is equal to 1.88×10^{-1} and 1.00×10^{-1} respectively, whereas $\overline{S_i^z}$ on inner sites are distinctly small and equal to 2.63×10^{-2} and 2.94×10^{-2} respectively. The fact that the magnitudes of $\overline{S_i^z}$ on inner sites for $J_2/J_1 \geq 0.3764$ are much smaller than those for $J_2/.J_1 \leq 0.3760$ demonstrates the disappearance of the Néel-like order. For intermediate J_2/J_1, on each corner site, $\overline{S_i^z}$ always keeps positive, and its magnitude is much larger than those of the inner sites. Such distribution results from spin disorder (spin liquid) behavior. In this case, the spins on corner sites are in a special status.

If J_2/J_1 increasing further, the *n.n.n.* interactions lead to the occurrence of a new ordered quantum phase. Fig. 3(d) shows the case of $J_2/J_1 = 0.88$. In subsystem B, the average value of positive $\overline{S_i^z}$ is 1.93×10^{-1}, and the fluctuation 4.67×10^{-3}. The four corner sites with negative $\overline{S_i^z}$ have the same value -1.37×10^{-1} due to the geometry of cluster (a). The distribution of $\overline{S_i^z}$ in subsystem B exhibits the AF Néel-like order. In subsystem A, $\overline{S_i^z}$ are very small and their average value is 5.11×10^{-3}. It does not means that the spin status is disordered. By contrary, it is also ordered by the calculation of $Q(\pi,0)$. A simple explanation to the smallness of $\overline{S_i^z}$ in subsystem A is given: cluster (a) consists of two subsystems A and B by J_1 coupling. It is noticed that subsystem B has odd sites, but subsystem A has even sites. If $J_1 = 0$, the distribution of $\overline{S_i^z}$ in subsystem B can be used to show the Néel picture from J_2 interactions. But, in subsystem A, we can not do it in the same way since $\overline{S_i^z} = 0$ exactly. For large J_2/J_1, the *n.n.n.* interactions dominate the physics of the cluster. Consequently, the site in subsystem A has small $\overline{S_i^z}$.

From our calculations, the following conclusions can be obtained. 1). although it has only 25 sites and nearly half of all sites on its boundaries, the molecular cluster (a) exhibits the obvious bulk behaviors. For small and large J_2/J_1, cluster (a) is in two different magnetic or-

dered phases. For the intermediate J_2/J_1, the spin status is disordered. Two kinds of quantum phase transitions take place around $J_2/J_1 = 0.3762$ and 0.612. respectively. 2). for cluster (a) with intermediate J_2/J_1, the spins on corner sites are in a special state. And their magnitudes of S_i^z are remarkably larger than those on inner sites. We think that the larger real cluster with the similar shape as cluster (a) will keep this character. 3). η plays an important role for real cluster to keep the bulk behaviors. Its increasing advantages the formation of bulk behaviors. From our calculations, we think that only for real clusters with η near 1, it is possible that there exists quantum phase transition around $J_2/J_1 = 0.38$.

It is somewhat surprise that the two critical values $J_2/J_1 = 0.3762$ and 0.612 of cluster (a) are very close to those of infinite square lattice $J_2/J_1 = 0.38$ and 0.60 [14]. The fact that the infinite $J_1 - J_2$ square lattice has the same $\eta = 1$ as cluster (a) may be responsible for the result. η is a key factor for real cluster to possess the similar phase diagram as that in infinite system. By using exact diagonalization, H. J. Schulz *et al.* studied the 6×6 cluster under the periodic boundary conditions. Their calculations show that there is no step-like change of $Q(\pi, \pi)$ around $J_2/J_1 = 0.38$, and $Q(\pi, \pi)$ becomes obviously small only when $J_2/J_1 > 0.6$ (see Fig. 3 (a) in Ref. [8]). To obtain reliable critical values of infinite system, one must resort to scaling analyses like doing in Ref. [8]. In addition, the 6×6 cluster has 56% sites on its boundaries. Although cluster (a) has remarkably fewer sites, the boundary effect might be weaker than the 6×6 cluster since it only has 46% sites on its boundaries. The real clusters with such shape as cluster (a) might be better choice than the conventional $n \times n$ cluster under periodic conditions to study some properties of the infinite $J_1 - J_2$ square lattice. But, the calculable sizes of the clusters with such geometric shape are only 13 and 25. It is difficult to obtain the results of infinite system by ordinary extrapolation since the scarcity of available points. One notices that the region ($0.3760 \sim 0.3764$) of J_2/J_1 of the real cluster of 25 sites, in which a step-like jump of $Q(\pi, \pi)$ takes place, is within that of the real cluster of 13 sites ($0.3381 \sim 0.3886$). We think that the J_2/J_1 region of the larger real cluster will fall into $0.3760 \sim 0.3764$. Then, we speculate that the critical value of the infinite system is $J_2/J_1 = 0.3762(\pm 0.0002)$. It may be more accurate than the previous result $J_2/J_1 = 0.38$.

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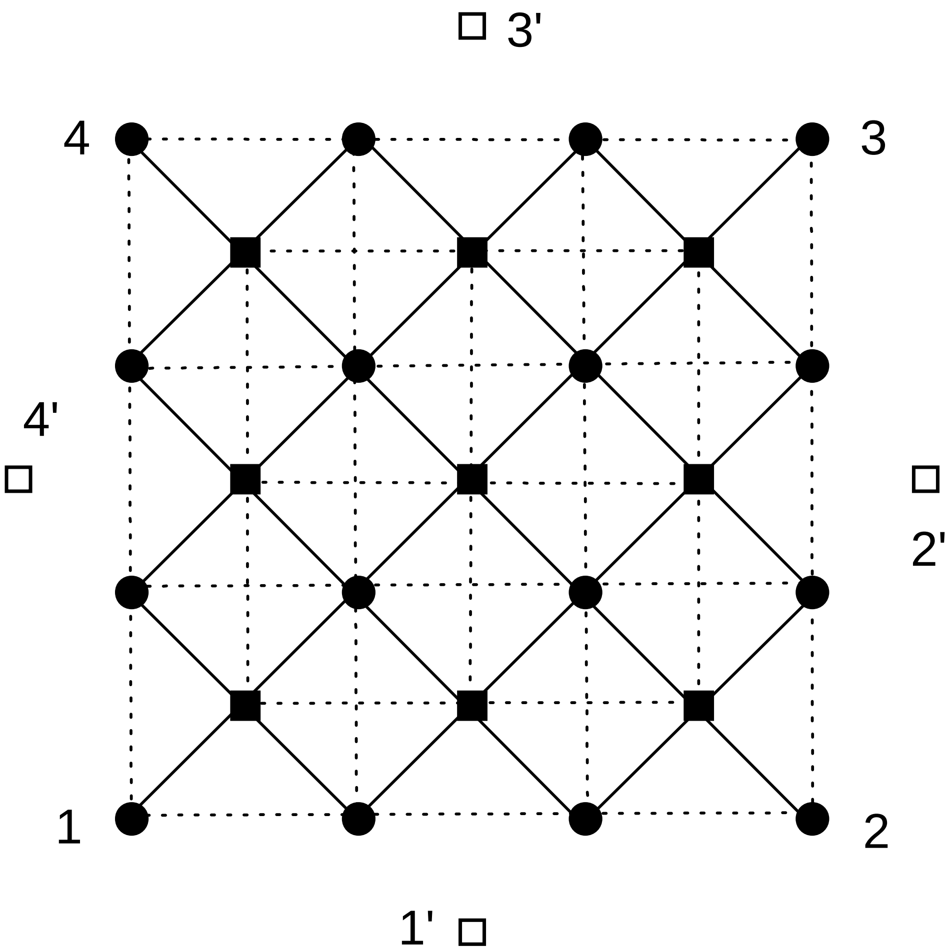
[16] The order of infinite system is uniform. But, for real cluster, it is nonuniform. Here, the word ‘order’ means a kind of bulk character of spin status.

FIG. 1. Five kinds of real clusters of 25 spins with different geometric shapes. All the sites except (a) $1'$, $2'$, $3'$ and $4'$, (b) 1, $2'$, $3'$ and $4'$, (c) 1, 2, $3'$ and $4'$, (d) 1, 2, 3 and $4'$, (e) 1, 2, 3 and 4 have 1/2 spin. The solid lines represent the *n.n.* interactions J_1, and the dot lines the *n.n.n.* interactions J_2. The cluster can be divided into two subsystems A and B. The solid circles denote the sites in A, and the solid and open squares those in B.

FIG. 2. $Q(\pi,\pi)$ and $Q(\pi,0)$ vs. J_2/J_1. Curves (a), (b), (c), (d) and (e) are $Q(\pi,\pi)$ for real clusters (a), (b), (c), (d) and (e) respectively (Fig. 1). Curve $Q(\pi,0)$ is for real cluster (a).

FIG. 3. Several kinds of $\overline{S_i^z}$ distributions on sites of cluster (a) (Fig. 1). The lengthes of arrows represent the magnitudes of $\overline{S_i^z}$. a) $\overline{S_i^z} = 0.236$ for the corner sites. b) $\overline{S_i^z} = 0.188$ for the corner sites. c) $\overline{S_i^z} = 0.100$ for the corner sites. d) $\overline{S_i^z} = 0.174$ for the center site.

Fig. 1 **By Yong-Jun Liu *et al.***



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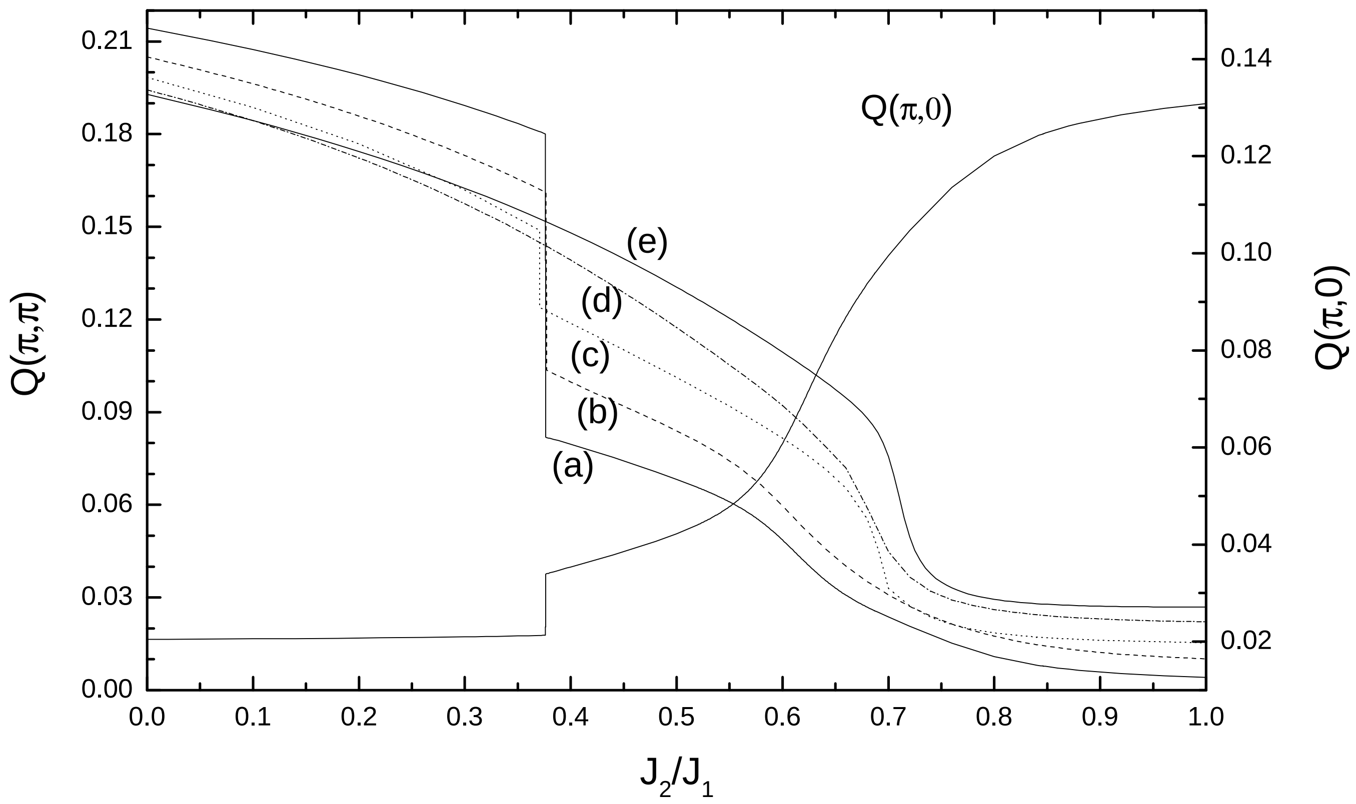

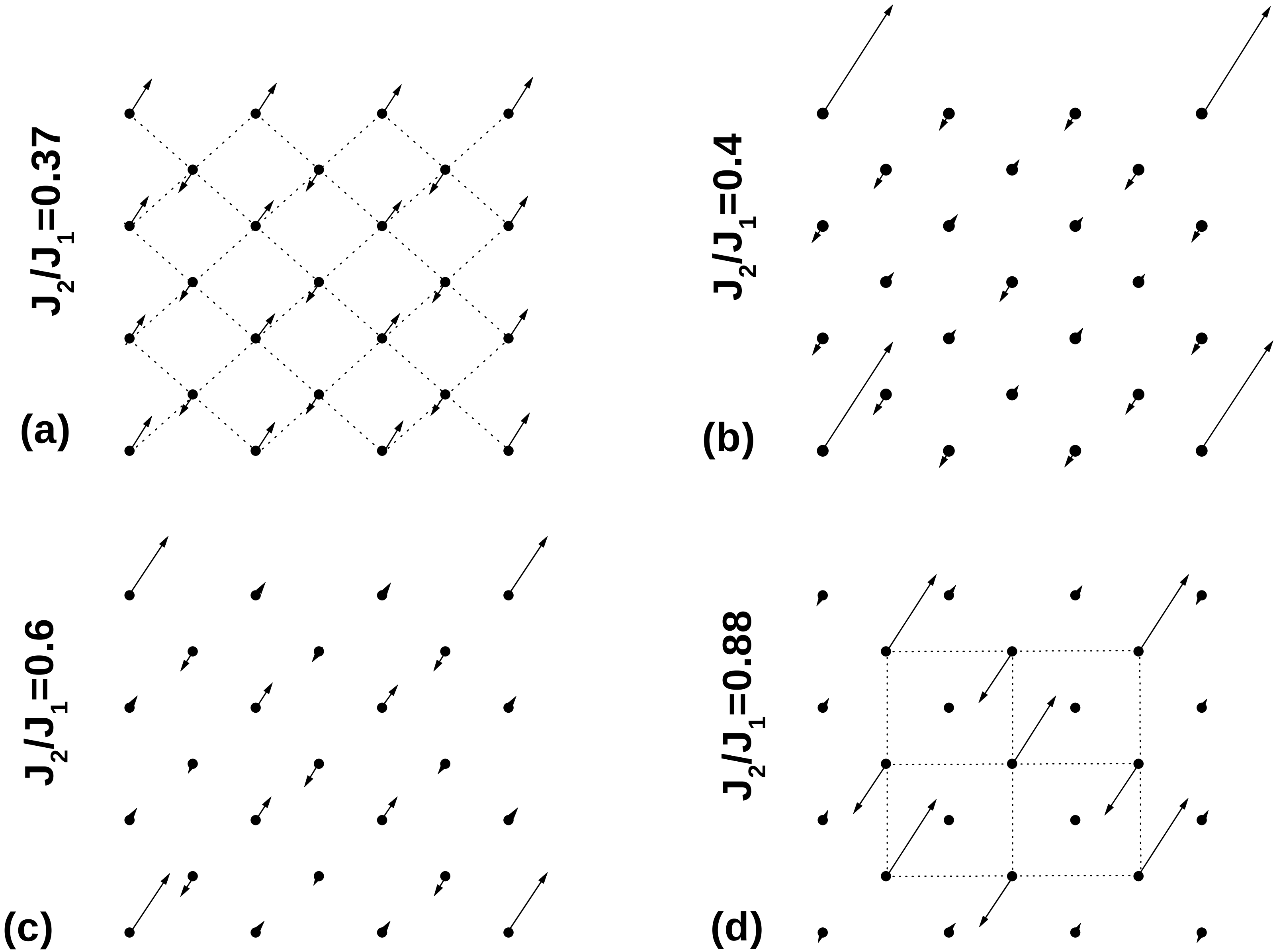

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